

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

0422

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1. REPORT DATE (DD-MM-YYYY) 21-11-2002		2. REPORT TYPE Final Technical Report		3. DATES COVERED (From - To) 01-08-1999 to 31-08-2001	
4. TITLE AND SUBTITLE Flexible Polymer LEDs using Lanthanide/Polymer Blends: A Route to Flexible Three-Color Displays				5a. CONTRACT NUMBER F49620-99-C-0055	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 65502 F	
6. AUTHOR(S) O'Regan, Marie, Dr.				5d. PROJECT NUMBER STTR	
				5e. TASK NUMBER TX	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIAx Corporation 6780 Cortona Drive Goleta, CA 93117					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 801 North Randolph Street, Room 732 Arlington, VA 22203-1977 Attention: Dr. Charles Lee					
11. SPONSOR/MONITOR'S REPORT NUMBER(S)					
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution Statement A. Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT PLEDs fabricated on flexible substrates offer advantages over the current standard glass substrates. Flexible display devices are lighter weight than their glass counterparts, fracture-resistant and have a thinner profile making them of particular interest for military land vehicle applications. Flexibility eases placement in instrument panels in tightly confined spaces, while resistance to fracture when accidentally struck by personnel is also a plus. Manufacturing costs should ultimately be lower than with glass substrates. The long-range goal of flexible 3-color displays offers the possibility of lightweight laptop computer screens and roll-up flat panel displays among other applications. During Phase II we increased the efficiency of the polymer/lanthanide blends by 20% over Phase I performance by the synthesis and incorporation into PLEDs of a new europium complex. We patterned more complex structures on plastic substrates and built, packaged and drove plastic yellow-green polymer displays with more than 6,000 pixels. Limited lifetimes kept blue and red emitting systems from being incorporated into the final plastic displays.					
15. SUBJECT TERMS PLEDs fabricated on flexible substrates, plastic substrates, resistance to fracture, flexible 3-color displays, lightweight laptop computer screens, roll-up flat panel displays, polymer/lanthanide blends, europium					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 38	19a. NAME OF RESPONSIBLE PERSON
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code)

Flexible Polymer LEDs using lanthanide/Polymer Blends

A Route to Flexible Three-Color Displays

Final Report

Phase II STTR Grant

Program Manager: Dr. Charles Lee, AFOSR

Contract period: August 1, 1999 – August 31, 2001



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Date: March 1, 2002

Contract no.: F49620-99-C-0055

Topic no.: AF98T007

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

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TABLE OF ABBREVIATIONS

Abbreviation	Full Form
LED	Light Emitting Display
PLED	Polymer Light Emitting Display
OLED	Organic Light Emitting Display
LCD	Liquid Crystal Display
PVDC	poly(vinylidene chloride)
Ln	lanthanide
PVK	Poly(N-vinylcarbazole)
CN-PPP	poly[2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene]
PET	Poly(ethylene terephthalate)
PLQE	Photoluminescence Quantum Efficiency
QE	Quantum Efficiency
PL	Photoluminescence
EL	Electroluminescence
ITO	Indium tin oxide

PROJECT OBJECTIVES

PLEDs fabricated on flexible substrates offer advantages over the current standard glass substrates. Flexible display devices are lighter weight than their glass counterparts, fracture-resistant and with a thinner profile. The first report of a flexible LED came from UNIAX in 1992ⁱ in the form of a simple alphanumeric display. Plastic displays are of particular interest for military land vehicle applications. The ability to be bent for placement in instrument panels in tightly confined spaces is attractive, while resistance to fracture when struck by personnel scrambling rapidly in or out of the vehicle is also a plus. Manufacturing costs should ultimately be lower than with glass substrates. Flexible 3-color displays, although a long-range goal, offer the possibility of lightweight laptop computer screens and roll-up flat panel displays among other applications.

SUMMARY OF RESULTS

During Phase II we have succeeded in increasing the efficiency of the polymer/lanthanide blends by 20% over Phase I performance, by the synthesis and incorporation into PLEDs of a new europium complex. The improvement was realized by increasing the conjugation of the ligand by an extra benzene ring. Given the difficulty in improving the lifetime of the blue emitting polymer we devoted effort to preparing a single component, spin castable lanthanide complex, through the optimization of a ligand system and targeted synthesis. The complex was designed to include structural features for optimizing charge transport across the bulk and to give the molecule topological attributes to discourage crystallization. The latter attribute enabled spin-casting of the molecule from solution, obviating the need to vapor deposit the material. This molecule had superior properties to the blue-emitting polymer used in Phase I. However, the lifetime was still shorter than desired.

We focused on patterning more complex structures on plastic substrates, during Phase II of the grant. Succeeding at this task, we were able to build, package and drive plastic displays with more than 6,000 pixels. We were not able to incorporate the blue and red emitting systems into

the final plastic displays because of the disappointing lifetime those systems showed. Thus, all the plastic displays are demonstrated using a yellow-green polymer.

PROJECT RESULTS

The research objectives in Phase II were:

- A. Blue-emitting polymer or spin-castable small molecule with superior properties to Phase I batch of CN-PPP
- B. Eu complex optimization
- C. Flexible substrate and Device Packaging

Note that sections I, II and IV (Part 1) were previously published as the 1st report on Phase II activities.

I. Blue-emitting polymer or spin-castable small molecule with superior properties to Phase I batch of CN-PPP.

At the beginning of Phase II work, we focused on polyfluorenes as a plausible alternative to CN-PPP for a blue emitting polymer. The reason for this choice was the vast body of work in the patent and peer-reviewed literature, as well as ongoing experience at UNIAX in synthesis and evaluation of polyfluorene polymers. One particular polyfluorene derivative was identified as promising for this project, polymer A. A batch of polymer A was prepared and purified, and devices built using it as the emissive polymer. The EL spectrum of a device built with this polymer is shown in Figure 1. As will be recalled from the Phase I and II proposals, the physical phenomena in operation (in photoluminance at least) in the lanthanide/polymer blend structure are that of Förster energy transferⁱⁱ from the conducting polymerⁱⁱⁱ to the ligand on the metal, followed by energy transfer from the ligand to the metal ion. The requirement for the conducting polymer is that there must be spectral overlap between the absorption spectrum of the metal complex and the emission spectrum of the conducting polymer. In practical terms, that means that there must be emission below 400 nm. Polymer A has a tail below 400nm, as does CN-PPP.

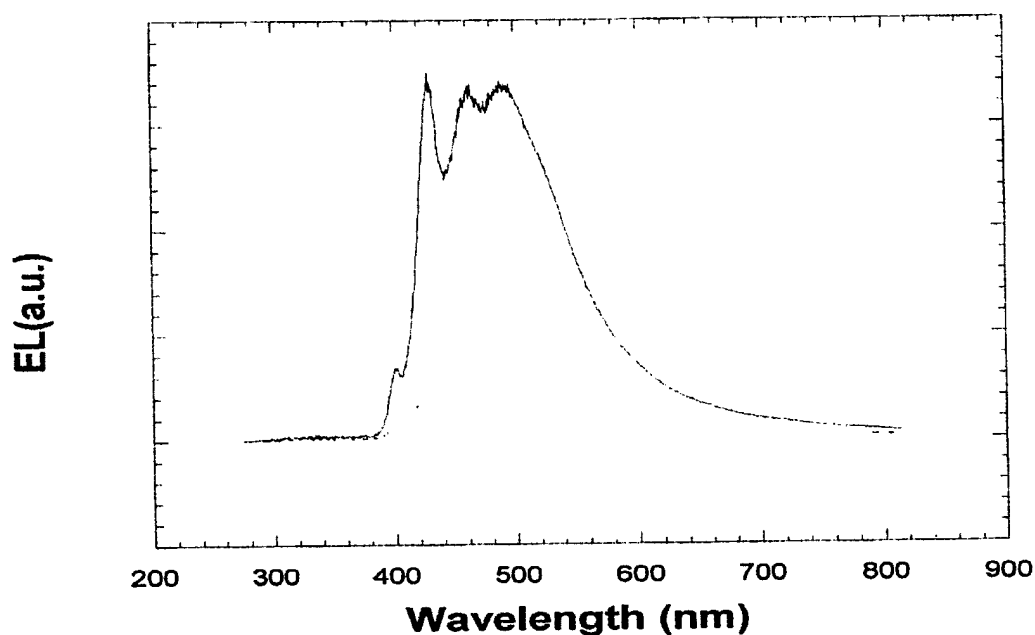


Figure 1. Electroluminescence spectrum of device built with polymer A.

After device architecture optimization, the device performance was compared to that of devices built with CN-PPP (with no Eu complex added to either formulation). The performance of polymer A was significantly better than that of CN-PPP, as shown in Figures 2 and 3, below.

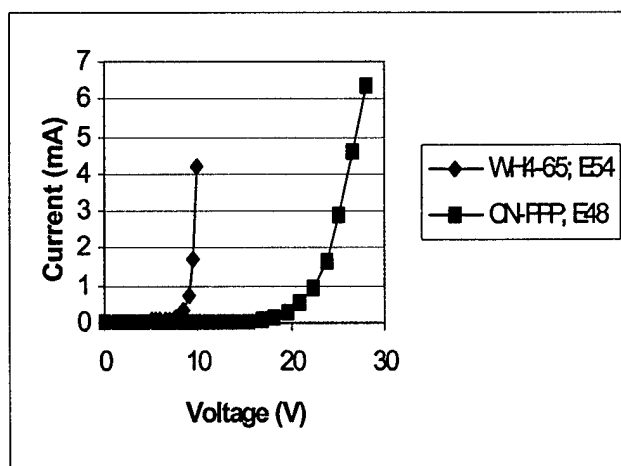


Figure 2. Comparison of i-v curves of devices built using polymer A (blue trace) and CN-PPP (magenta trace).

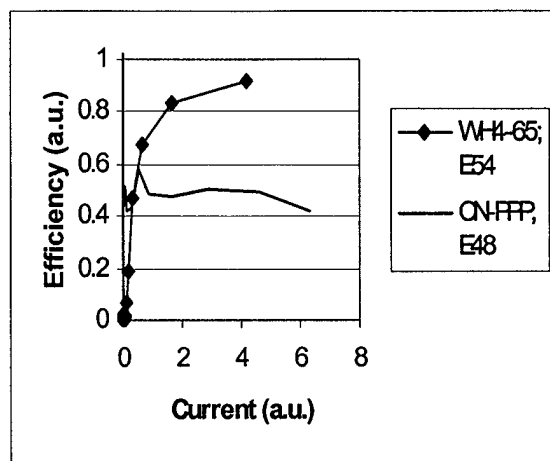


Figure 3. Comparison of device efficiency using CN-PPP or polymer A as the emissive polymer layer.

The turn-on voltage for polymer A is significantly lower than that for CN-PPP, as may be seen in Figure 2. This is an important attribute, as is the approximately 2x increase in device efficiency that polymer A devices exhibit, when compared with CN-PPP.

The next step was to determine whether energy transfer took place with polymer A and Eu complexes, and to what extent. To that end, tris(dinaphthoylmethane)(monophenanthroline)europium, hereafter called Eu(2-2), was added in varying amounts to the solution of polymer A, and devices built. The EL spectra of devices with 5 wt.%, 10 wt. % and 20 wt. % Eu(2-2) complex in polymer A are shown in Figure 4.

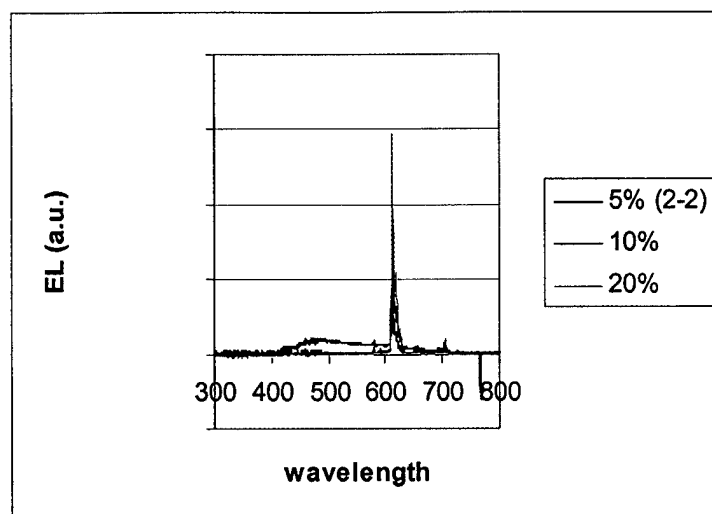


Figure 4. EL spectra from devices containing emissive layers of 5-20% Eu(2-2) in polymer A.

Notice that at 5% loading, the emission from the conducting polymer has not been entirely quenched, making the emission appear pink to the human eye. At the higher loadings of 10 and 20% lanthanide complex, polymer emission is completely quenched and the light emitted is pure red. Device data are shown in Figures 5 and 6.

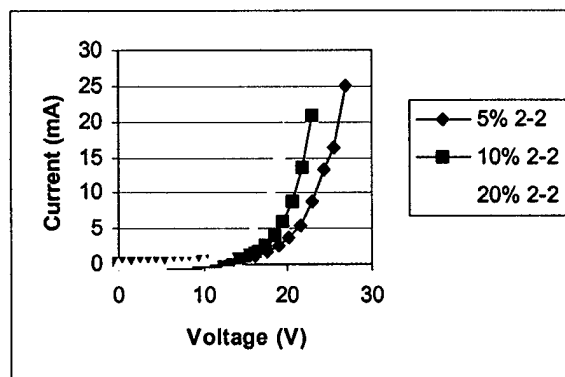


Figure 5. i-v curves from devices made with 5-20 % Eu(2-2) in polymer A as the emissive layer.

The turn-on voltage increases somewhat with the addition of the lanthanide complex, as was also observed in the lanthanide/CN-PPP blend devices. However, the increase is not as pronounced, and the effect is lessened by the fact that polymer A has a lower turn-on voltage than CN-PPP.

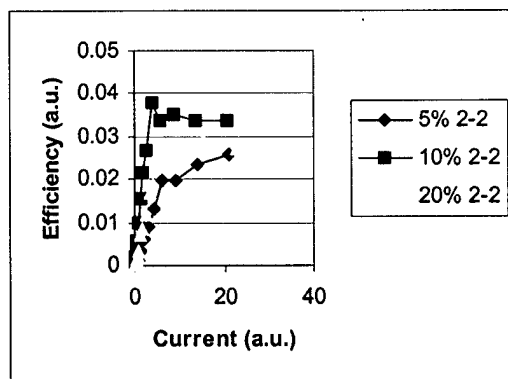


Figure 6. Efficiency data from devices made with 5-20 % Eu(2-2) in polymer A as the emissive layer.

Unfortunately, addition of the lanthanide complex results in a significant decrease in light output and device efficiency. This decrease is very disappointing, given the superior performance of polymer A. We postulate that the degree of overlap of the polymer emission with the absorption band of the ligand on the lanthanide is insufficient to allow efficient transfer. Thus, while polymer A is a superior blue-emitting polymer to CN-PPP in all other respects, the greater degree of overlap of CN-PPP with the lanthanides is currently unmatched.

Under the auspices of another government project, some parallel work at UNIAX has also been focused on blue emitting polymer, with the goal of a full-color polymer LED. We have monitored those activities with this project in mind, seeking a better blue-emitting polymer. Polymers under evaluation incorporate polyfluorene or spiro cores. To date, none of the polymers identified as promising have emission at or close to 2.6 eV, i.e. suitable for overlap with the ligand system of the lanthanide complex. The emission spectra of the blue polymers evaluated may be seen in Figure 7, showing no emission below 400nm. (Figure 7 is taken from the quarterly report for the DARPA flexible emissive displays project).

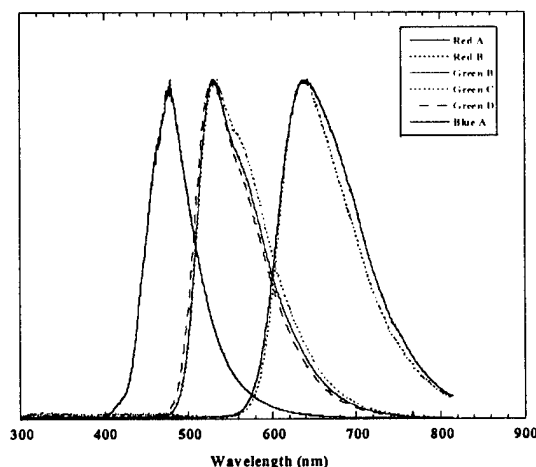


Figure 7. Emission spectra for devices fabricated from six experimental polymers

Thus, we continue to use CN-PPP and have improved the yield and purity of the polymer. In parallel, as discussed below, we are focused on spin-castable Eu complexes, in an effort to eliminate the polymer while retaining the advantages of spin-casting versus vacuum sublimation. The advantages of this approach are obvious: elimination of the low lifetime polymer, retention of the processing advantages of spin-casting and simplification of the device-making procedure.

II. Eu complex

1. Improvement of the lanthanide complex for blending with host polymer

At the end of Phase I, the best performance was obtained by blending the host polymer, CN-PPP, with tris(dinaphthoymethane)(monophenanthroline)europium (III), Eu(2-2). During Phase II we have succeeded in increasing the efficiency of the polymer/lanthanide blends by 20% over Phase I performance, by the synthesis and incorporation into PLEDs of a new europium complex.

We postulated that an increase in electron delocalization (i.e. increased aromaticity) on the ligand framework would result in better electron transport through the layer, and hence in lower

operating voltage and increased efficiency. During Phase I, the best efficiency was obtained using tris(dinaphthoylmethane)(monophenanthroline)europium (III) (1) blended with CN-PPP. In designing an increase in aromaticity we needed to be aware of the concomitant lowering of the band gap. For instance, tris(dianthraoylmethane)(monophenanthroline)europium (III) has a lower lying triplet level than Eu(III) and no red emission is observed from a blend of the complex with CN-PPP. We decided to prepare tris[1-(phenanthroyl)-1-(naphthoyl)methane](phenanthroline)europium (III), hereafter called Eu(3-2), in an effort to improve the efficiency of the blend LEDs.

PLED devices were prepared using a blend of 2 wt. % of Eu(3-2) with CN-PPP as the emissive layer. At 2 wt.% loading only emission from the Eu ion was observed, as evidenced by the EL spectrum, shown in Figure 8.

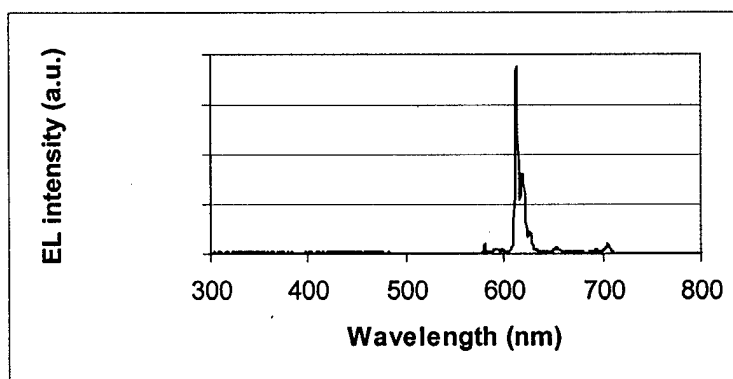


Figure 8. EL spectrum from a device where the emissive layer comprises 2 wt. % Eu(3-2) in CN-PPP.

The device turn-on voltage (see Figure 9) was three volts lower than for the best blend device prepared during Phase I, although the turn-on voltage is still characteristically higher for the blend device than for the host polymer-only device.

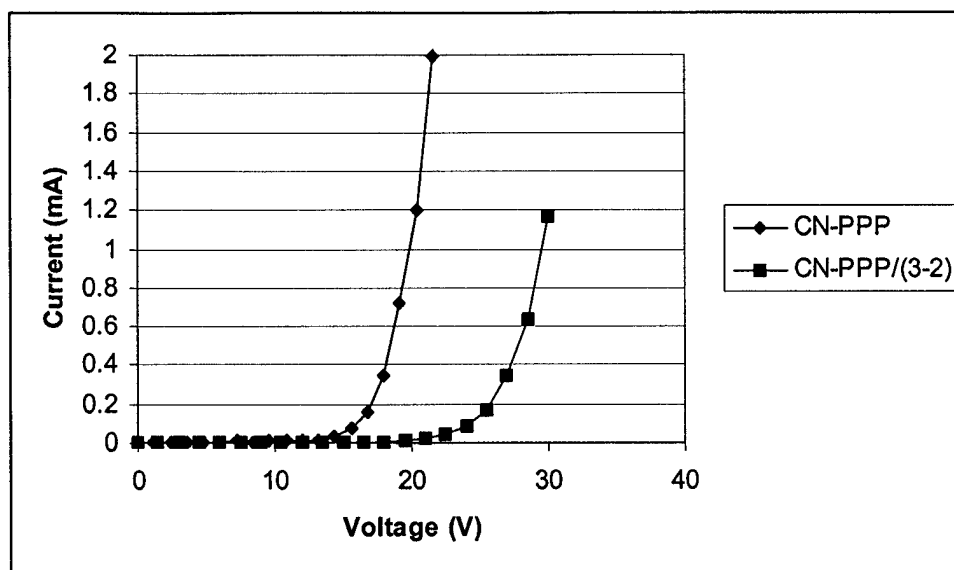


Figure 9. *i-v* characteristics of devices made with CN-PPP and CN-PPP blended with two different Eu complexes.

Most interesting is that the efficiency of a CN-PPP/Eu(3-2) device was 20% higher than that of a CN-PPP/Eu(2-2) device, as shown in Figure 10. Thus, Eu(3-2) replaces Eu(2-2) as the best lanthanide complex for blending with CN-PPP to get pure red emission.

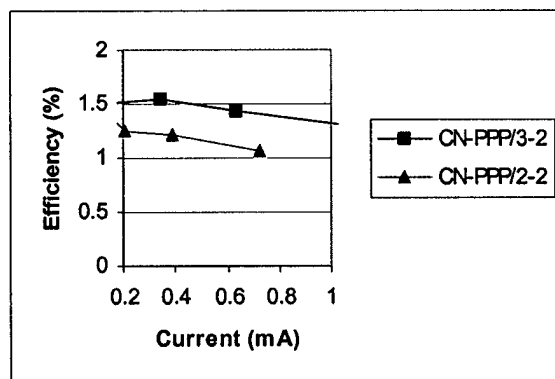


Figure 10. Comparison of efficiencies of blends of CN-PPP with Eu(2-2) or Eu(3-2).

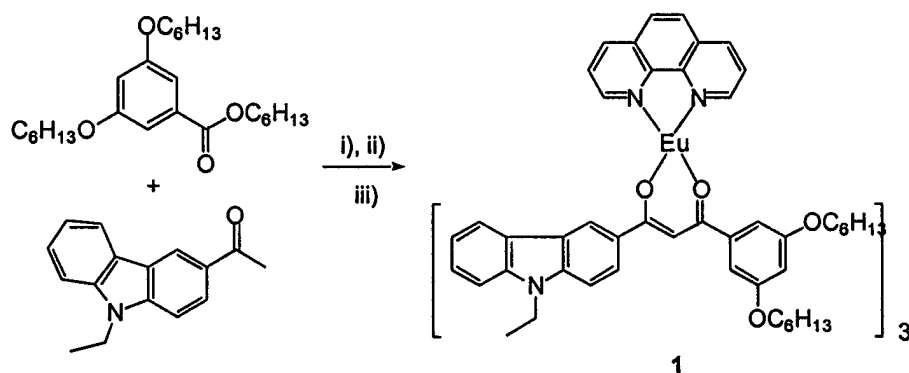
2. Single-component, spin-castable Eu complex

Due to the difficulty in identifying a replacement polymer for CN-PPP, we are also focused on spin-castable Eu complexes. The strategy here was to eliminate the need for a host polymer that

emits below 400 nm, while retaining the advantages of spin-casting the active device layers. The complex targeted was tris[1-(N-ethylcarbazolyl)-1-(3',5'-hexyloxybenzoyl)methane][phenanthroline]europium. Hereafter it is designated Eu(SC).

. It was postulated that synthesis of aromatic β -diketonate ligands having long and/or branched alkyl chains should meet the high energy triplet state requirement, allow for spin-casting of a neat film, and eliminate the need for a blue-emitting host polymer. The complex was designed to include structural features for optimizing charge transport across the bulk and to give the molecule topological attributes to discourage crystallization. The latter requirement was incorporated so as to obtain amorphous films directly from solution. The phenanthroline ligand was included since it is thought to be an electron transport functionality.^{iv} A carbazole fragment was appended to the diketonate ligand with the intention of improving hole transport.^v Finally the hexyloxy groups were introduced to prevent crystallization and to increase solubility in common organic solvents.

The synthetic pathway followed is shown in Scheme 1.



Scheme 1

Scheme 1. Synthetic route to tris[1-(N-ethylcarbazolyl)-1-(3',5'-hexyloxybenzoyl)methane][phenanthroline]europium

As shown in Scheme 1, the diketonate ligand is prepared by Claisen condensation of 3-acetyl-9-ethylcarbazole^{vi} and hexyl-3,5-hexyloxybenzoate in the presence of NaH. After refluxing in dimethoxyethane for 24 hours, followed by acetic workup and purification by chromatography,

one obtains 1-(N-ethylcarbazolyl)-1-(3,5-hexyloxybenzoyl)methane in 24 % yield. The europium complex, Eu(Sc) is prepared by taking advantage of well-established protocols.^{vii} Deprotonation of three equivalents of 1-(N-ethylcarbazolyl)-1-(3,5-hexyloxybenzoyl)methane with excess NaOH, followed by treatment with $\text{EuCl}_3(\text{H}_2\text{O})_6$ and finally phenanthroline affords Eu(Sc) in 50% yield. Pure complex is achieved by precipitation from a concentrated acetone solution. The complex shows (by DSC) a glass transition temperature at 65°C and powder diffraction experiments show no evidence of crystalline regions. The morphological properties make it possible to cast clear transparent films directly from solution and the thickness of these films can easily be controlled by the solids loading of the solution and spin.

The absorption spectrum shows an absorption onset at about 458 nm, corresponding to a HOMO-LUMO gap of 2.71 eV. This value is also observed in the spectrum of the sodium salt of the diketonate ligand, meaning that light absorption is controlled by the ligand framework. The sharp emission at 612 nm in the photoluminescence spectrum is characteristic of the europium ion within a tris β -diketonate/phenanthroline environment. Therefore, the triplet level of the ligand is sufficiently high to allow energy transfer to the ion.^{viii} Use of an integrating sphere revealed that the solid state photoluminescence efficiency from films of Eu(Sc) is 50 (3) %, which is extremely high. These measurements were made using the 351 nm line from an argon laser (intensity of 2.5 mW/cm²), an integrating sphere, a high pass filter that blocks the laser line, and a silicon diode.^{ix}

Two types of LED structures were fabricated that incorporated Eu(Sc), according to methodology described in Yang et al.^x In the first, a film of Eu(Sc) (600 Å) was spin cast directly onto the anode, indium tin oxide (ITO). The solution from which the film was cast was 1 % wt./volume in toluene and was filtered through a 5 micron Nylon filter. The layer of Eu(Sc) was subsequently dried under vacuum at ambient temperature for approximately 1 hour. The calcium cathode layer, overcoated with aluminum was deposited as described previously.^x This device has only a single layer and only one molecular component between the electrodes, corresponding to the simplest architecture possible. Light emitted from this device shows a 3.5 nm bandwidth emission centered at 614 nm.

The turn-on voltage for current and luminance is observed at 5.3 V (8.8 mV/Å), as shown in Figure 11. This value is similar in magnitude to many polymer LEDs and lower than many multi-layer organic LEDs (OLEDs). These characteristics demonstrate that the ligand design was successful in facilitating electron and hole injection and transport into and across the europium layer.

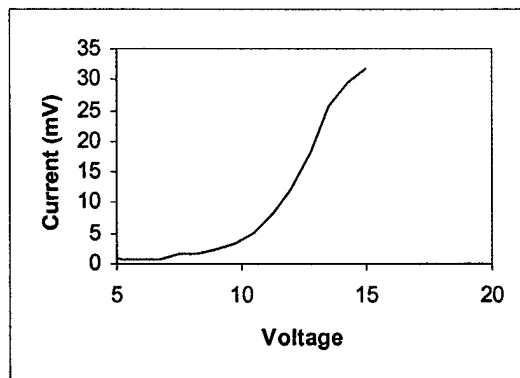


Figure 11. *i-v* characteristics of a single-layer, single component PLED made with Eu(Sc)

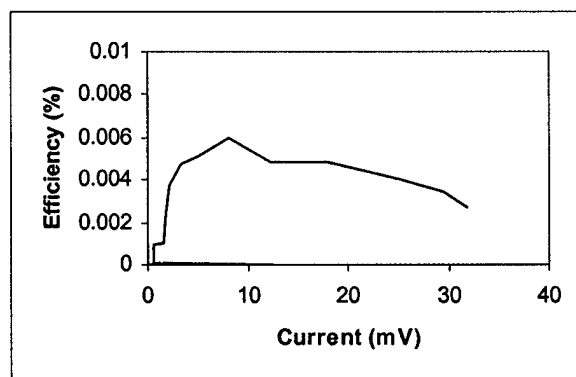


Figure 12. Efficiency of the single-layer, single component PLED made with Eu(Sc)

At 3 mA, the light output is only 9 cd/m² with an external EL quantum efficiency of 0.08%. Since the device efficiency of the single layer device is quite low (see Figure 12), a second device structure was targeted in an effort to improve device efficiency, and to get insight into the mechanism of europium electroluminescence. In this type of device, a layer of PVK (30 nm) was first spin-cast from a 2% solution of PVK in 1,1,2,2 - tetrachloroethane on top of ITO and, after drying at 60 °C for 1 hour, an 700 Å layer of Eu(Sc) was spin-cast as before. The cathode layer is the same as in the single layer device. Only emission from Eu was observed, as expected. Figure 13 shows the current-voltage curve for this device.

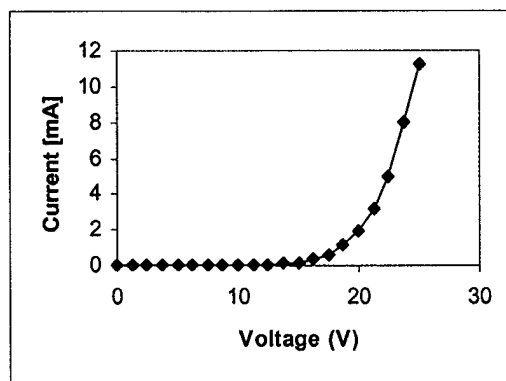


Figure 13. *i-v* characteristics for device type 2: ITO/PVK/Eu(Sc)/Ca/Al

Compared to the single layer device, the turn-on voltage is higher, ca. 8.75V (8.75 mV/Å), due to the extra thickness introduced by the PVK layer; both devices operate at equivalent field strengths. Despite the increased voltage, device efficiency was improved considerably (50 cd/m² at 3 mA) with an external quantum efficiency of 0.3 %.

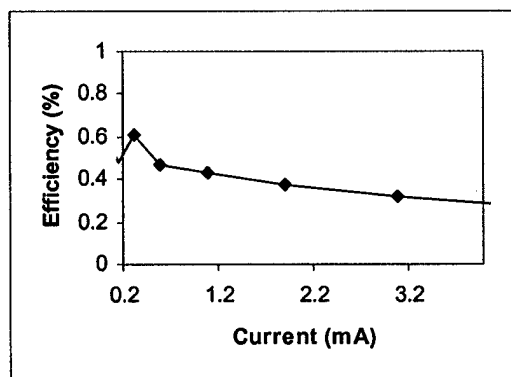


Figure 14. Device efficiency of device type 2: ITO/PVK/Eu(Sc)/Ca/Al

Thus, incorporation of the PVK layer into the device structure has resulted in a 4-fold increase in light output over the single layer device. It is thought that the PVK layer acts as a hole injection and electron blocking layer^{xi} facilitating more balanced carrier injection from the anode and cathode.

In this work, we have shown that it is possible to introduce structural attributes to the ligand framework of an europium complex that allow its use as the electroluminescent layer in a single component LED. The key design components include the use of hole and electron transport

fragments for facilitating charge transport, together with aliphatic groups that lead to a stable amorphous phase. The film forming properties of Eu(Sc) play an important role in facilitating device fabrication.

III. Progress at on new materials synthesis and understanding during second year of Phase II funding.

(The following section was written by Dr. Vojislav Srdanov, co-Principal Investigator)

The STTR project "Flexible polymer LEDs fabricated from spectrally pure lanthanide/polymer blends: A route to flexible 3-color displays" was funded following the discovery that the blue-emitting CN-PPP LED starts to emit in the red spectral region (612 nm) if blended with an organometallic Europium compound.¹ Phase II of this project included the following three objectives to be carried out at UCSB:

- I. Synthesis of a more durable blue-emitting conjugated Polymers or Oligomers.**
- II. Solving the Injection Problem of blue emitting LEDs.**
- III. An attempt to produce a green-emitting LED based on a Tb³⁺ compound.**

As will be discussed below, the team was not successful in the synthesis of a blue-emitting polymer that was longer lived than CN-PPP. Thus, another task was added to the effort:

II. Determination of the critical parameters for efficient energy transfer in Ln/Polymer blends

In addition to this task, the chemical stability of the lanthanide complexes in liquid and solid phases were examined, in terms of their sensitivity to solvent polarity, light, heat, and moisture. The results of these investigations are reviewed below.

Task I. Synthesis of a more durable blue-emitting conjugated Polymer or Oligomer

It is well known that the most difficult challenge currently faced in the area of PLED emissive materials is synthesis of a bright, long lived polymer that emits blue light. Many groups around the world are focused on this issue.

From the original work of Yang et al.,² it was known that the blue-emitting LED made using CN-PPP polymer had an external ELQE on the order of 1.4 % , and a turn-on voltage between 7 V and 15 V depending on the percentage of hole-transporter (TPB) in the blend. The device life-time was not reported in the original paper² but was found during this study to be relatively short, on the order of an hour or less. Comparable electro-luminescence quantum efficiencies were found for CN-PPP and Eu/CN-PPP LEDs indicating an efficient polymer-

lanthanide energy transfer, but the persistently short device life-time pointed again on the poor chemical stability of the CN-PPP polymer. Because of that, new blue-emitting polymers was sought.

The blue-emitting conjugated polymers involved in this study, obtained from various

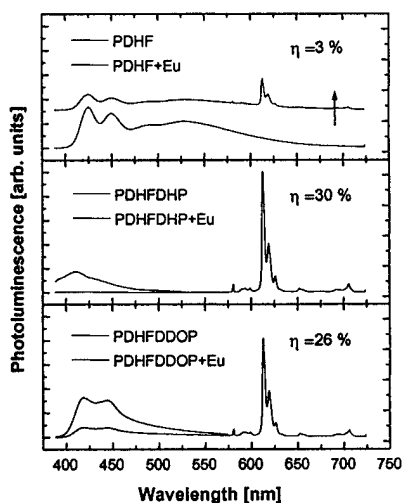
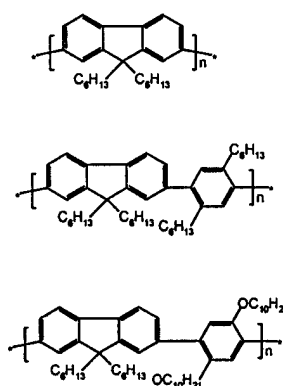


Fig. 15. PL spectra of some blue-emitting polymers before and after blending with Eu(2-2)₃Phen complex



sources, were blended with Eu-compounds and tested for electro-luminescent properties by UNIAX corporation. In parallel to this effort, researchers at UCSB have synthesized small quantities of several other blue-emitting polymers of the type shown in Figure 15. These were also blended with Europium complexes and tested for energy transfer by PLQE and spectrally resolved photoluminescence. Like in the case of Eu/CNPPP blends where energy transfer is

quite efficient, blending blue-emitting polymers with Eu-complex should result in a complete quenching of the polymer luminescence with simultaneous appearance of a strong $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission. Unfortunately, with the exception of PDHFDHP shown in Figure 15, no other blue-emitting polymer has fulfilled this basic requirement. Further investigation of the Eu/PDHFDHP blends showed no improvements over Eu/CN-PPP ones.

Task II.

Determination of critical parameters for efficient energy transfer in Ln/Polymer blends

Energy transfer in lanthanide/polymer blends, depicted schematically in Figure 16, proceeds in two major steps:

- (i) Energy transfer from the polymer to the ligand
- (ii) Energy transfer from the ligand to the lanthanide cation

The overall efficiency of the energy transfer is measured by the quantity known as Luminescent Quantum Efficiency, (LQE) given by the ratio between the number of emitted and absorbed photons in case of photo-excitation, or as a ratio between the number of emitted photons and the number of injected electron-hole pairs in the case of electro-luminescence. While the details of the energy transfer from the polymer to the ligand may depend on

Polymer \rightarrow Ligand \rightarrow Lanthanide

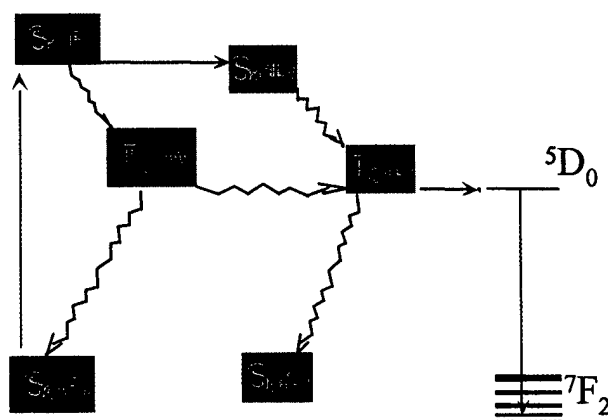


Fig.16. Energy transfer diagram of the lanthanide/Polymer blends

the type of excitation (optical versus electrical), the transfer from the ligand to the lanthanide cation is

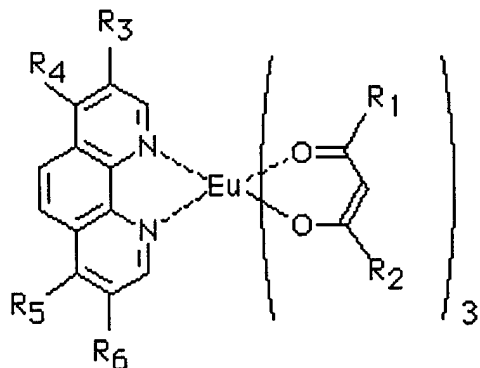


Fig. 17. Europium $\text{Eu}(\text{ligand})_3\text{Phen}$ complexes used in these studies

independent of the excitation mechanism. Below we present the results related to the optimization of the second step, i.e. the energy transfer from the ligand to the lanthanide cation.

The type of lanthanide complex explored in this study is shown in Figure 17. For all the compounds, hydrogen was substituted at R₃ through R₆ positions, whereas the R₁ and R₂ groups were varied. Two of the following four groups were attached at the R₁ and R₂ positions: Methyl (0), Phenyl (1), Naphthyl (2), Anthryl (3). The number in parentheses represents the number of phenyl rings in R₁ and R₂. Five such Eu compounds, 1-0, 1-1, 2-2, 2-3, and 3-3, have been synthesized and evaluated for energy transfer. As is known from the early studies of Crosby and coworkers,⁵ efficient ligand-to-metal energy transfer in lanthanide complexes requires a good overlap between the triplet state of the ligand and the lowest spin-orbit component of the first excited electronic state of the lanthanide cation. In some cases, like ours, one can vary conjugation length of the ligand and, in this way, the energy of the ligand triplet state with respect to the electronic states of the lanthanide cation. By changing the conjugation length in a systematic manner, one should ideally be able to “walk through” the Crosby resonance, which would be indicated by a maximum in the PL quantum yield at a certain conjugation length. As shown in Figure 18, this is what was found in the experiment, in which the Eu(2-3)₃Phen compound showed higher PLQY than the “neighboring” Eu(2-2)₃Phen and Eu(3-3)₃Phen.

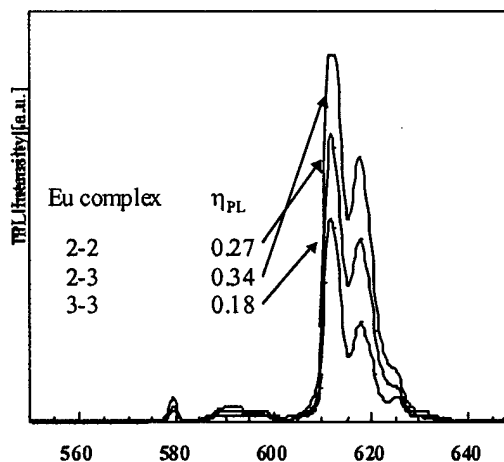


Fig. 5. Normalized (to the same absorbance) PL spectra of the three Eu(ligand)₃Phen near the Crosby resonance.

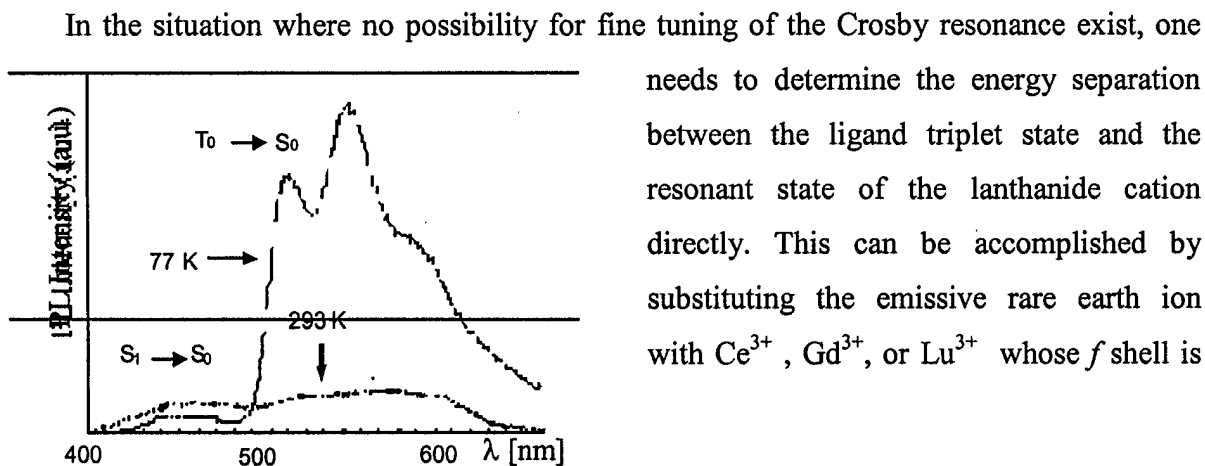


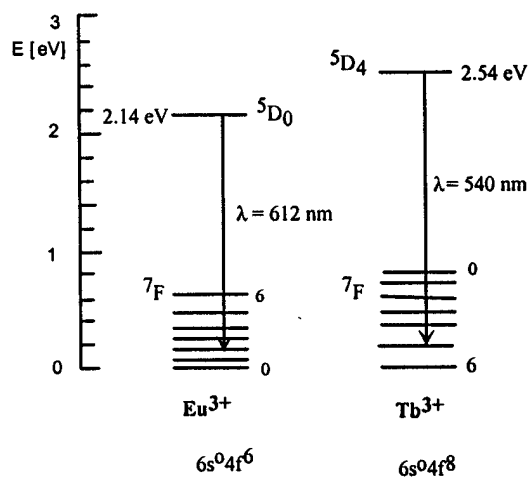
Fig. 6. PL spectra of Gd(M1)₃Phen at room temperature and at 77 K.

In the situation where no possibility for fine tuning of the Crosby resonance exist, one needs to determine the energy separation between the ligand triplet state and the resonant state of the lanthanide cation directly. This can be accomplished by substituting the emissive rare earth ion with Ce³⁺, Gd³⁺, or Lu³⁺ whose *f* shell is

empty, half filled, and completely full, respectively. In either case, the lowest excited electronic state of these ions is well above the ligand triplet state so no ligand-to-metal energy transfer is possible. In such cases the excited ligand triplet state may give rise to phosphorescence, particularly if nonradiative quenching is suppressed by lowering the sample temperature. Indeed, as shown in Figure 6, lowering the temperature greatly enhances (and hence identifies) the spin-forbidden, ligand-centered, singlet-triplet emission. Assuming that the short-wavelength hump corresponds to rovibronic 0-0 transition, the ligand triplet level is found at 2.43 eV, a 0.3 eV above the Eu emissive 5D_0 state.

Task III: An attempt to produce a green-emitting LED based on a Tb^{3+} compound

Even though organic electro-luminescent devices utilizing Terbium complexes have been produced in the past,⁶ attempt to observe such luminescence with the Tb-complexes utilizing the same β -dicetonate ligands reviewed in the previous section, gave no positive results. As shown in Figure 19, the possible reason for this may be the higher energy of the Tb^{3+} 5D_4 level, which lies 0.4 eV above the analogous Eu^{3+} 5D_0 level. This requires correspondingly higher energy of the ligand triplet state, otherwise no energy transfer can occur.



Task IV: Chemical stability of the lanthanide complexes

The existing lanthanide complexes are all Ln^{3+} cations to which three single-charged organic ligand-anions are chelated: $Ln_3^+(Ligand^-)_3$. For the most part, the complex is held together by Coulomb forces with a small covalent contribution arising from back-donation of the

ligand electron density to the empty 5d orbital of the lanthanide cation. The electrostatic nature of the bonding makes lanthanide complexes susceptible to polar solvents whose molecules can remove organic ligands from the lanthanide cation. This was confirmed by the series of experiments in which the PL spectra of the Eu(2-2)_3 compound were recorded in different solvents. As shown in Figure 8, the Eu(2-2)_3 energy transfer occurs in

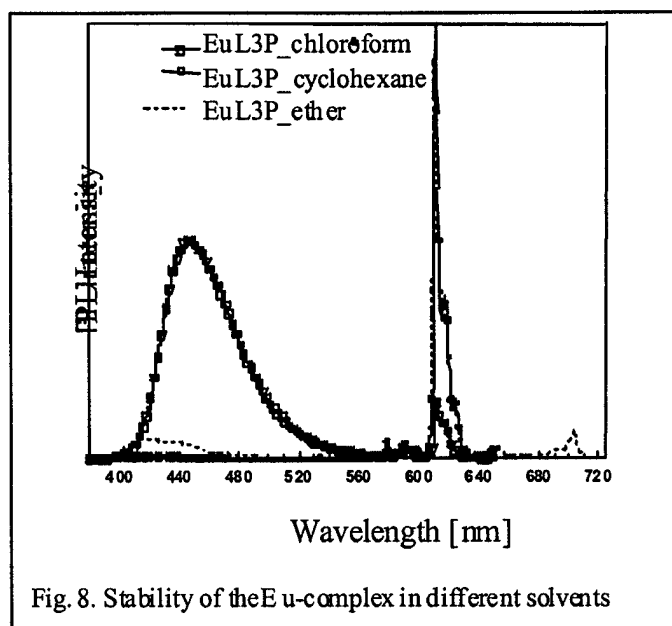


Fig. 8. Stability of the Eu-complex in different solvents

ether and cyclohexane but not in chloroform, which is more polar than the other two solvents. The nearly absent Eu luminescence in chloroform we take as an indication of chemical destruction of the lanthanide complex.

Another issue concerns chemical and physical stability of the lanthanide complexes and the Ln/polymer blends to light, moisture and oxidation. In a series of experiments we found that $\text{Ln}_3^+(\text{Ligand})_3$ complexes have a sharp damage threshold in respect to the absorbed radiation. The threshold varies from case to case, but it can be said with certainty that 100 mW/cm^2 (and higher) of 360 nm radiation causes irreparable damage to the Eu(2-2)_3 compound. Indeed, as shown in Figure 9, the integrated PL intensity of the neat Eu(2-2)_3 thin film with optical density of 1 increases linearly with the input radiation until 100 mW/cm^2 is reached and then it starts to fall behind. If the constant input-power above the damage threshold is chosen, the PL decays in

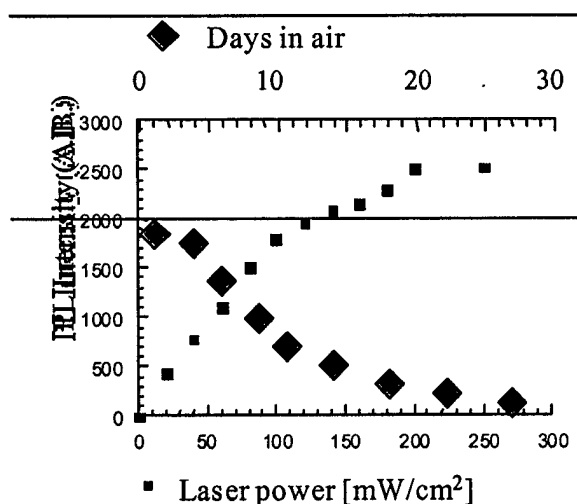


Fig. 9, Photoluminescence spectrum of the Lanthanide complex with aging and as a function of the laser input power

time exponentially. Important to note is that the threshold for radiation damage is the same in air and in inert atmosphere, hence ruling out photo-oxidation. The probable cause of the observed behavior is excessive heat, which develops as a result of the difference in energy ($h\nu$) between absorbed and emitted photons, even if

PLQE = 1. For PLQE < 1 the problem is aggravated further by the heat released due to non-radiative quenching of the excited state. In the case of a hypothetical Europium complex with PLQE = 1, we calculate that each absorption event releases 1.42 eV of energy, thus raising "local" temperature of to 18, 000 K. Such an extreme heat (if not quickly dissipated) can thermally dissociate the lanthanide complex, resulting in the decay of the emissive material. Heat dissipation is also required in lanthanide LEDs because of their small ELQE and high operating voltages. Because of this, LEDs based on lanthanide/polymer blends, where polymer matrix acts as a heat sink, may have a better chance for success than OLEDs with the emissive layer containing a neat lanthanide compound.

If protected from ambient light but left exposed to air, the PLQE of the spin-coated neat thin film of Europium complexes decreases on a daily basis. The same occurs with the europium complexes diluted in PMMA and/or CN-PPP, but with a much slower decay rate. This suggested intercalation of oxygen and/or water molecules, which somehow interfere with the Europium emission. Rare earths ions are known to reduce

($\text{Ln}^{3+} \rightarrow \text{Ln}^{2+}$) in the presence of reactive species, a possibility we considered. Needless to say, Eu^{2+} has completely different set of electronic states (quite similar to Gd^{3+}), which precludes the ligand-metal energy transfer. Another possibility was the quenching of Eu^{3+} emission by water molecules. In order to distinguish between two possibilities, we performed temperature-dependent magnetic susceptibility measurements on the Europium complex before and after its prolonged exposure to air. As shown in Figure 10, the results were almost identical indicating that no change in the Eu^{3+} oxidation state has occurred. Due to the difference in ground state symmetry, the magnetic moment of Eu^{2+} is exactly 2.4 times larger than that of that of Eu^{3+} , the difference easily recognized in the magnetic susceptibility measurements. This leaves us with the quenching of Eu PL by intercalated water as the most plausible explanation.

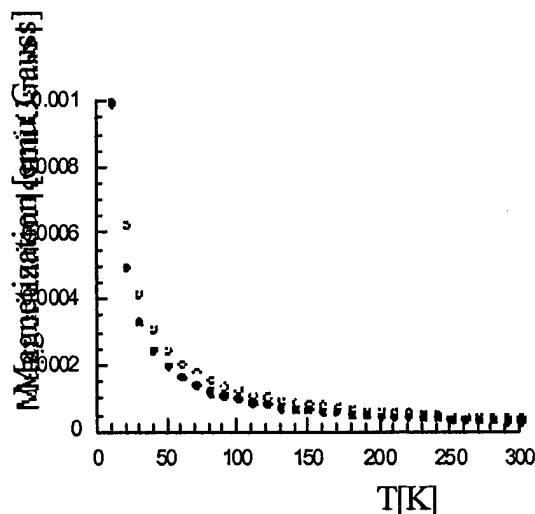


Fig. 10. Magnetic susceptibility of the $\text{Eu}(\text{MI})_3\text{Phen}$ compound after synthesis (open circles) and after 1 Monte in air.

IV. Plastic Substrate and Device Packaging – Part 1

In parallel to the emissive materials synthesis efforts, work is ongoing to elucidate processing conditions for flexible substrates as well as to identify and test suitable barrier substrates. This area of effort is a major focus going forward. Plastic substrates and device packaging go hand in hand because we plan to use the barrier substrate as a lid for the PLED (of course, without the ITO).

The idealized structure of a polymer LED built on a plastic substrate is illustrated in Figure 15.

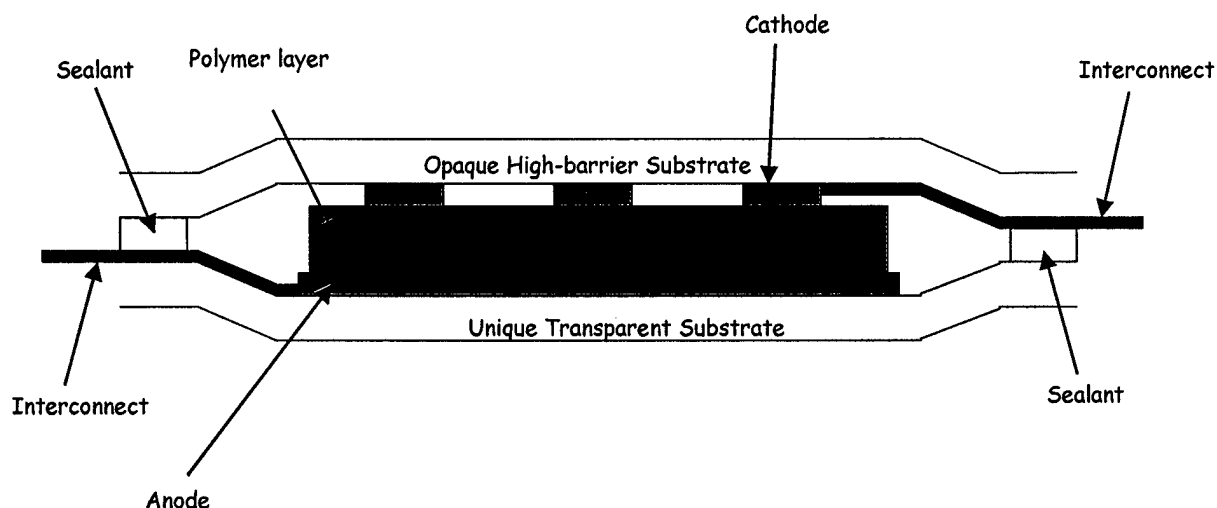


Figure 15. Schematic of the structure of a PLED built on a plastic substrate.

The most severe challenge has been the identification/fabrication of a suitable barrier substrate. Remember that the diffusion of ambient water and oxygen through the plastic substrate negatively impacts device lifetime. Barrier substrates for PLEDs need to exclude water and oxygen to the tune of $< 1 \times 10^{-6}$ g/m²/day. Note that the limit for WVTR and OTR measurements by MOCON or any other method is 10^{-3} g/m²/day. A typical plastic substrate has WVTR / OTR of 25-100 g/m²/day, which is obviously unacceptable.

A number of changes have taken place at UNIAX since the writing of the last report. Due to the acquisition of the company by DuPont, we now have access to the ongoing work at DuPont in barrier materials for OLEDs. UNIAX has also been awarded another government contract, from

DARPA, for the development of full color, flexible emissive displays. Thus, in this program, we are able to leverage the knowledge gained in the DARPA program, and use those learnings in pursuit of our goals.

Many people have focused on using inorganic layers as barriers for plastic substrates. The first place this has been done is in the food packaging industry. Performance of these barriers does not have to be as good as OLEDs require, since a potato chip bag needs barrier properties of about $1.5 \text{ g/m}^2/\text{day}$. Focus has been on using inorganic layers as barriers, since a pinhole-free inorganic coating is impervious to oxygen and water vapor. However, it is very difficult to achieve such a perfect inorganic coating on a plastic film. In practice, there is a certain density of defects and pinholes present. For example, table 1 shows MOCON readings for a number of films:

Table 1. WVTR for a number of inorganic coatings on PET.

<i>Film id</i>	<i>WVTR (g/m²/day)</i>
PET	212
PET/SiO _x	7.7
SiO _x /PET/SiO _x	0.29

Note: Data in Table 1 are taken from Tropsha , J. Phys. Chem. B 101 (1997)

As part of the Phase II work, we are evaluating barriers from as many sources as possible, internal and external to the company. One of the experiments we planned in the Phase II proposal was to coat such inorganic layers on the plastic substrate. We have found, by coating both thin and thick inorganic layers, that neither is sufficient to protect the PLED built on that substrate from water and oxygen attack. This finding is consistent with the data shown in Table 1, given the fact that the PLED needs WVTR and OTR less than $10^{-6} \text{ g/m}^2/\text{day}$.

DuPont has a program in the area of plastic barriers for OLEDs that predates the acquisition of UNIAX. We are now working together in evaluating these barriers and building PLEDs on them. Our strategy has been to evaluate barriers in isolation as much as possible, i.e. keeping all other parameters constant. The way we accomplished this is to build a display on a glass substrate, and then encapsulate the display with the barrier material. A glass substrate/glass lid device is used as

the control. We then evaluate the light output of the displays over time to understand the efficacy of the barrier. Since we wished to keep as many parameters as possible constant in our evaluation of barrier materials, we made the decision to use as active layers polymers with which we have a lot of experience. For us that means using the yellow-green emissive polymer shown in Figure 21. The advantages of using this material are that we have a lot of lifetime data with this polymer on glass substrates, under glass processing conditions, and we understand the degradation mechanism of the polymer better than that of CN-PPP. As we move to the end of the program, we will attempt to merge these parallel paths, building a Eu device on a plastic barrier substrate.

By the method described above, we have screened substrates from commercial sources as well as internally built barriers. Figure 20 shows an example of the type of data collected. The yellow area is a lit pixel of a polymer LED. Over time, the emission degrades due to failures in the barrier layer.

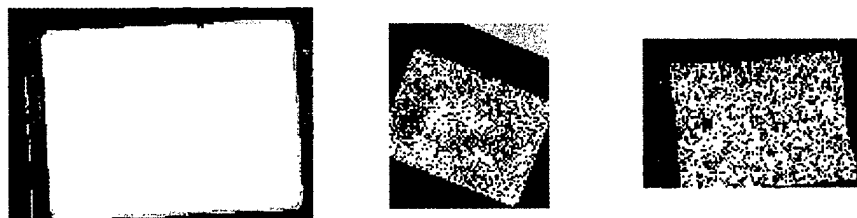


Figure 20. Degradation of a pixel over time due to inadequate barrier properties (glass substrate/plastic lid)

Figure 21 shows a comparison of device lifetime with devices built on glass substrates and either glass or plastic barrier lids.

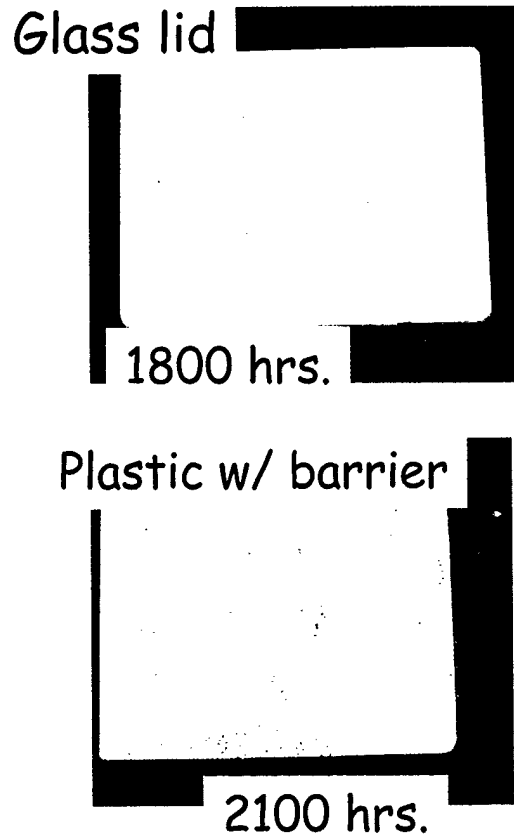


Figure 21. Top: Pixel lit from a PLED built on a glass substrate, encapsulated with a glass lid, after storage for 1800 hours at room temperature.

Bottom: Pixel lit from a PLED built on a glass substrate, encapsulated with a plastic barrier lid, after storage for 2100 hours at room temperature.

It may be seen from Figure 21 that the performance of the plastic barrier lid is very good, although not as good as glass yet. If one looks closely at the bottom photo, you can see a number of small black spots, caused by penetration of moisture or oxygen through the lid. However, contrast this performance with the device shown in Figure 22, which shows a PLED built on a glass substrate and using as a lid a piece of plastic with no added barrier properties.

Plastic lid, no barrier

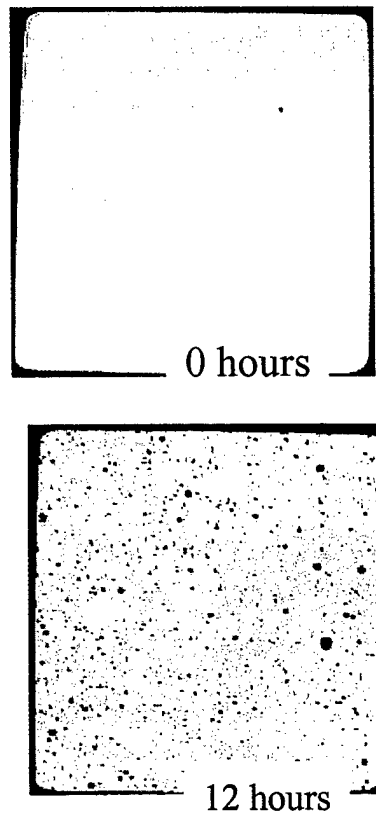


Figure 22. Performance of PLED device built on a glass substrate with a plastic lid that has no added barrier properties. This device is stored at high temperature, and high humidity conditions.

Work is ongoing under the auspices of the DARPA program to pattern plastic substrates for building cell phone and larger size displays. We will leverage from that patterning work when we build our plastic displays.

IV. Plastic Substrate and Device Packaging – Part 2

Work during Phase II has been focused on developing the processes needed to build pixelated displays on plastic substrates. The samples we built on plastic substrates during Phase I were relatively simple, since they were segmented displays, and did not require metal patterning beyond shadow masking. Many more processes had to be developed in order to allow us to build larger, more complex plastic displays. We have leveraged other work going on in the company,

funded both by DARPA and by internal funds in order to develop these processes. Figure 23 below shows the patterning processes generally required for a pixelated display.

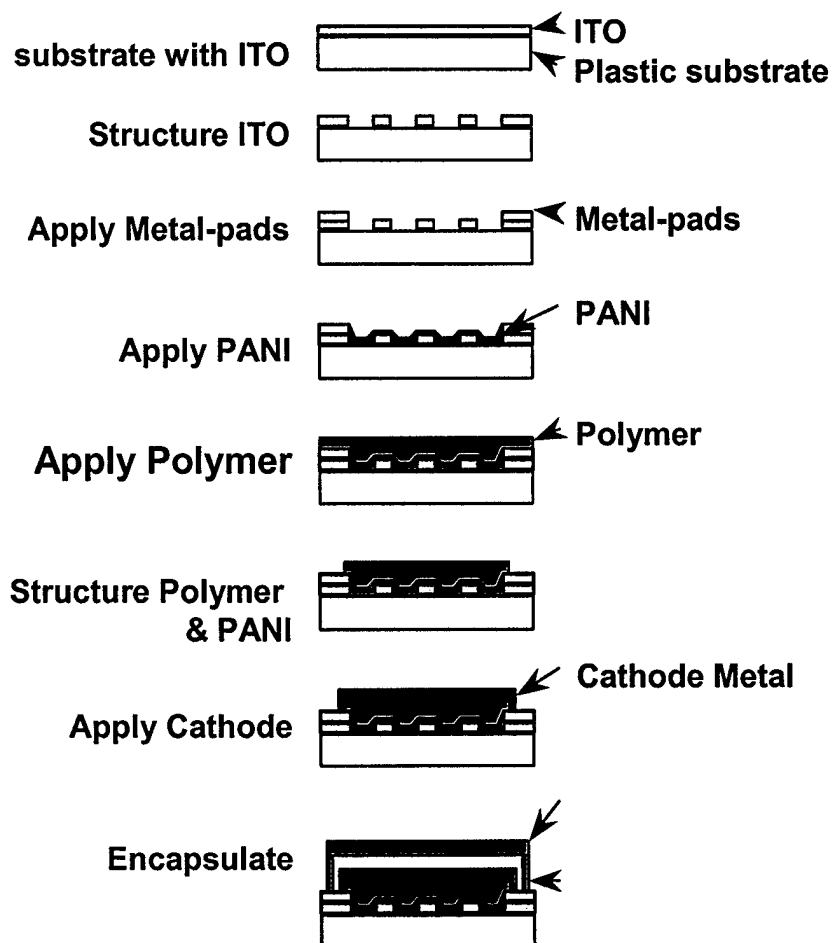


Figure 23. Sequence of steps required to pattern a substrate for use in a PLED device.

The patterning required for PLED substrates involves standard semiconductor-type wet etch chemistry. For plastic substrates, we have had to adapt these processes significantly from those used on our glass displays, changing temperatures, chemicals and handling procedures.

The first area of focus was on the plastic substrate itself. We struggled with the unacceptably high defect density on commercially available ITO-coated plastic substrates. Such defects are acceptable in the industry that uses the material today, and include inclusions, catalyst residue and other particles. Examples of commonly observed defects in commercially available, optical grade, material are shown below.

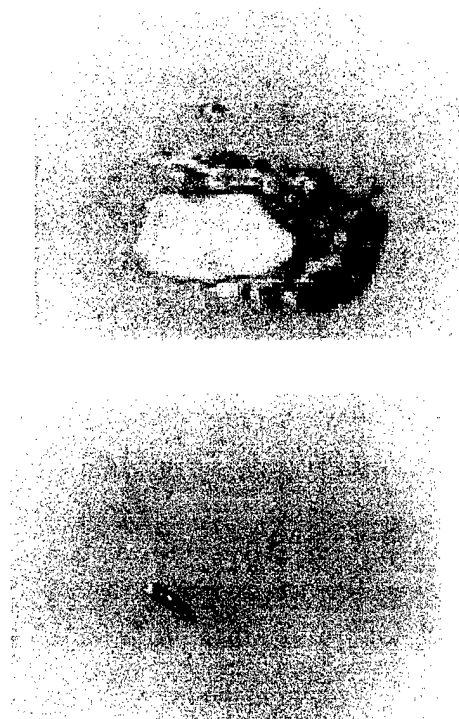


Figure 24. Examples of commonly observed defects in commercially available ITO-coated plastic substrates.

An example of the issues raised by these defects is shown in Figure 25, below.

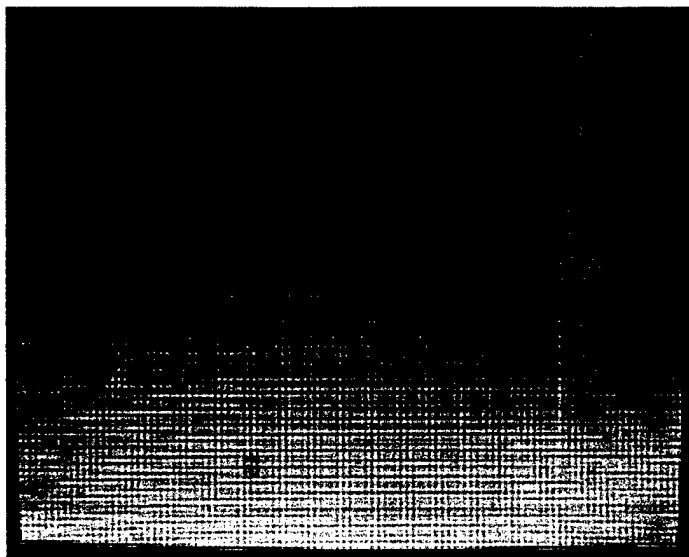


Figure 25. Example of the defects caused in a display by particulate contamination in the plastic substrate.

One column in the display is incompletely lit, although addressed, because of a break in the ITO. It is not known (for this particular display) what is the cause of the break. Typically, such cracks are caused by particles embedded in the plastic, resulting in incomplete ITO coverage.

In order to address this issue, we formed a JDA with another company to focus on improving plastic substrates. We are now receiving the first optimized samples from manufacturing-scale runs of these substrates. We will not show any displays built on these substrates in this report, since we have just received the bare substrates, but we are optimistic that they will yield greatly improved displays. Our reason for optimism is that the inspection data indicate much smoother surfaces, with greatly reduced particle counts. The improved plastic substrate also has a higher temperature tolerance than the existing commonly used substrate (PET), which will also allow us more processing latitude in patterning and building displays. The higher Tg substrate will also be evaluated, in a separate program, for use as an active matrix backplane substrate. The temperatures required for active matrix backplanes are considerably higher than those for the passive displays being fabricated at the moment.

As indicated by Figure 23, work was intensely focused on building pixelated displays on plastic substrates during Phase II. We began by building 100 pixel displays, as shown in Figure 26.

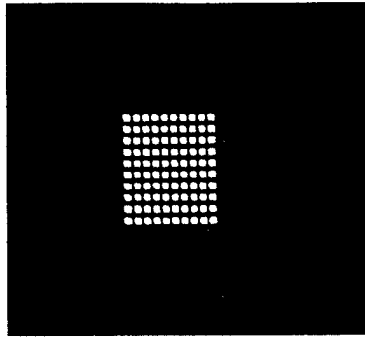


Figure 26. 100 pixel display, built on a plastic substrate.

As the patterning processes were developed, we expanded the pixel count to a 96x64 design, with more than 6,000 pixels. The challenges involved in this step included extra patterning steps, layer to layer alignment issues (registration) and polymer spinning uniformity. Layer to layer registration is an issue for plastic substrates, because all plastic substrates move upon exposure to elevated temperature. An example of the issue is shown below, in Figure 27.

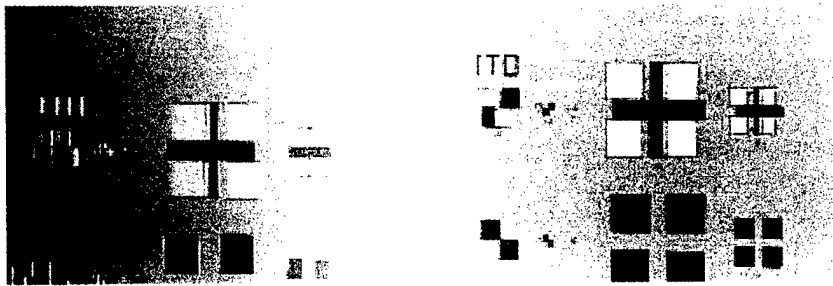


Figure 27. Left and right sides of a six inch substrate, showing the misalignment of ITO and metal layers (squares and cross).

In the case of Figure 27, the middle of the substrate was aligned correctly, and one can see the resulting misalignment at each side. We worked to build in processing latitude for the layer to layer variation using compensation artwork. Work was also done to optimize the metal deposition temperature, minimizing it as much as possible, to reduce CTE movement. While we are still working on optimizing layer to layer registration as much as possible, we have improved it enough so that we can routinely build cell phone sized displays.

We packaged a pixelated display built on plastic using thin film deposition and epoxy coverage for encapsulation. Photographs of the display are shown below, in Figure 28.

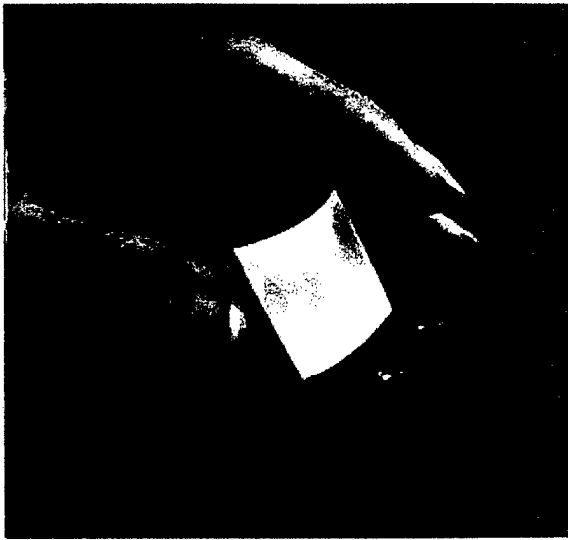


Figure 28. Plastic display shown at SID'01.

Since the performance of the blue emitting polymers continued to disappoint, we did not build blue and red emitting displays on plastic substrates. We continue to work on blue emitting polymers both internally and with external partners, since this is critical for full color displays.

CONCLUSIONS

We focused on patterning more complex structures on plastic substrates. Succeeding at this task, we were able to build, package and drive plastic displays with more than 6,000 pixels. Work on the barriers for plastic substrates advanced considerably during the program, so that we could demonstrate plastic displays for long periods of time. Unfortunately, we were not able to incorporate the blue and red emitting systems into the final plastic displays because of the disappointing lifetime those systems showed. Thus, all the plastic displays are demonstrated using a yellow-green polymer.

On the emissive materials front, we have succeeded in increasing the efficiency of the polymer/lanthanide blends by 20% over Phase I performance, by the synthesis and incorporation into PLEDs of a new europium complex. The improvement was realized by increasing the conjugation of the ligand by an extra benzene ring. Given the difficulty in improving the lifetime of the blue emitting polymer we devoted effort to an alternate path, preparing a single component, spin castable lanthanide complex, through the optimization of a ligand system and targeted synthesis. The complex was designed to include structural features for optimizing charge transport across the bulk and to give the molecule topological attributes to discourage crystallization. The latter attribute enabled spin-casting of the molecule from solution, obviating the need to vapor deposit the material. This molecule had superior properties to the blue-emitting polymer used in Phase I. However, the lifetime was still shorter than desired.

EXPERIMENTAL DETAILS

The synthesis of tris[1-(N-ethylcarbazolyl)-1-(3',5'-hexyloxybenzoyl)methane](phenanthroline) Europium has been described in the body of the report. CN-PPP was prepared using the methods described by Yang et al.⁹ Polystyrene and PVK were used as received from Aldrich. All of the polymer films used in the photoluminescence experiments were prepared by spin casting chloroform solutions of the polymer and Eu complex onto glass substrates.

Absorption spectra were measured with a Shimadzu UV-2401 PC UV-VIS recording spectrophotometer. For the photoluminescence spectrum measurements, the 351 line from an argon ion laser was used as the excitation source; neutral density filters were used to set the pump intensity to 0.1 mW/cm^2 . The emission was spectrally dispersed by a 50 cm focal length monochromator with a 150 lines/mm grating and detected by a CCD camera. The response of the spectrometer was calibrated by measuring the blackbody spectrum from a tungsten halogen lamp (Ocean Optics LS-1). All measurements were performed in air, but samples were stored in vacuum. The total time of exposure to air was always kept to less than five minutes to avoid photooxidation.

Quantum efficiency measurements were made using the 351 nm line from the argon laser, an integrating sphere, a high pass filter that blocks out the laser line, and a silicon diode. The laser intensity was 2.5 mW/cm^2 . The technique was similar to those reported on previously by deMello and Greenham.^{xii,xiii}

The photoluminescence lifetime measurements were made using 10 ns pulses from a Nd:YAG laser as the excitation source ($\lambda = 355 \text{ nm}$). The photoluminescence was dispersed by the Acton monochromator described above and detected by a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier tube was detected by a digital oscilloscope. The fluorescence decays were fit to the equation $I = I_0 \exp(-t/\tau)$, where τ is the photoluminescence lifetime.

The procedure for making LEDs is described in the body of the report. Film thicknesses were measured by a Tencor profilometer. Current-voltage and light-voltage curves were measured using a Keithley 236 source-measure unit and a calibrated silicon diode. EL spectra were measured using an Oriel Multispec monochromator with a CCD camera.

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Dr. Hailing Wang, UNIAX	Research Chemist
Dr. Vojislav Srdanov, UCSB	Researcher, co-Principal Investigator
Mr. Matthew Robinson, UCSB	Graduate Student
Ms. Ana Misic, UCSB	Undergraduate student

PUBLICATIONS RESULTING FROM PROJECT

Synthesis, Morphology and Optoelectronic Properties of Tris[1-(N-ethylcarbazolyl)-1-(3',5'-hexyloxybenzoyl)methane](phenanthroline) Europium. Matthew R Robinson, Marie B. O'Regan, Guillermo C. Bazan, *Chem. Commun.*, 2000, 1645.

Science and Technology Concentrates, *C & En News*, August 28, 2000.

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